PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-067000
(43)Date of publication of application : 05.03.2002

(51)Int.Cl. B82B 1/00
B82B 3/00

(21)Application number : 2000-259414
(22)Date of filing : 29.08.2000

(71)Applicant : NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL & TECHNOLOGY
TOMITA PHARMACEUTICAL CO LTD

(72)Inventor : MAKITA YOJI
IGAI OSAMU
OI KENTA
OKUBO AKIRA
HASHIMOTO NOZOMI

(54) METAL NANOWIRE AND METAL NANOPARTICLE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide metal nanowire and metal nanoparticles, and a manufacturing method thereof without using a mold or fine processing technique.
SOLUTION: A method for manufacturing nanowire and/or nanoparticles consists of irradiating with an electron beam on metal nanowire supported by a carrier at one end thereof and a metal ion carrier.

LEGAL STATUS
[Date of request for examination] 13.09.2000
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the

examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number] 3409126
[Date of registration] 20.03.2003
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] The metal nano wire by which the end was supported by support.
[Claim 2] The nano wire according to claim 1 whose metal nano wire is a silver nano wire.
[Claim 3] The manufacturing method of the metal nano wire which irradiates an electron ray at metal ion support, and/or metal nano particle.
[Claim 4] The manufacturing method according to claim 3 which irradiates an electron ray at complex ion support, and manufactures a silver nano wire and/or silver nano particle.
[Claim 5] Complex ion support is general formula [1]:AgaBcDeSifPgOh. [1] [B is at least one sort chosen from alkali metals, an alkaline-earth-metal element, copper, zinc, hydrogen, and ammonium, and D is at least one sort chosen from from among the metallic elements which can become the metal ion of 3 - pentavalence. Moreover, the subscripts in a formula are $0<a$, $0<=c$, $1<a+c<=4$, $1<=e<=2$, $0<=f<=3$, $0<=g<3$, and a number that fills $10<=h<=15$.] The manufacturing method according to claim 4 which is the compound come out of and shown.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a metal nano wire, metal nano particle, and those manufacturing methods.
[0002]
[Description of the Prior Art] It is known that a metal nano wire will be used as a template of an electron device ingredient or a carbon nanotube. Conventionally, in the carbon nanotube, since a metal nano wire was manufactured within the rill of a silica, and on a film, it has manufactured inevitably only the nano wire of the gestalt which used the carbon nanotube, the silica, and the film as mold. For example, the powder of the silica which has a slot on the nano-scale was suspended and agitated in the EtOH-H2O solution containing AgNO3, and although the silver nano wire was obtained by heat-treating, it depended for the gestalt of this wire on the gestalt of the slot which a silica has. Moreover, although the golden nano wire using ultra-fine processing technology is also known, a setup of processing conditions is difficult for processing the gold of a nano unit, and it is difficult to manufacture a nano wire easily like this invention.
[0003]
[Problem(s) to be Solved by the Invention] This invention aims at offering a metal nano wire, metal nano particle, and those manufacturing methods, without using mold or ultra-fine processing technology.
[0004]
[Means for Solving the Problem] this invention person found out that a metal nano wire and metal nano particle were obtained, without needing mold by irradiating an electron ray at metal ion support, as a result of repeating examination wholeheartedly in view of the trouble of the above-mentioned conventional technique.
[0005] That is, this invention offers the following metal nano wire, metal nano particle, and those manufacturing methods.
The metal nano wire by which the term 1. end was supported by support.
A nano wire given in the term 1 whose term 2. metal nano wire is a silver nano wire.
The manufacturing method of the metal nano wire which irradiates an electron ray at term 3. metal ion support, and/or metal nano particle.
A manufacturing method given in the term 3 which irradiates an electron ray at term 4. complex ion support, and manufactures a silver nano wire and/or silver nano particle.
Term 5. complex ion support is general formula [1]:AgaBcDeSifPgOh. [1]
[B is at least one sort chosen from alkali metals, an alkaline-earth-

metal element, copper, zinc, hydrogen, and ammonium, and D is at least one sort chosen from from among the metallic elements which can become the metal ion of 3 - pentavalence. Moreover, the subscripts in a formula are $0<a$, $0<=c$, $1<a+c<=4$, $1<=e<=2$, $0<=f<=3$, $0<=g<3$, and a number that fills $10<=h<=15$.] A manufacturing method given in the term 4 which is the compound come out of and shown.

[0006]

[Embodiment of the Invention] In this invention, a metal nano wire and metal nano particle are manufactured by irradiating an electron ray at metal ion support. Although what a metal nano wire and/or metal nano particle generate when the metal ion supported by metal ion support is returned by the exposure of an electron ray, that action mechanism becomes a metal, and that metal comes out from support to the external world and develops is conjectured, this invention is not limited to this guess.

[0007] Especially as a metal of a metal nano wire, although not restricted, silver, palladium, nickel, gold, etc. are mentioned.

[0008] The metal nano wire of this invention is a nano wire with which the end was supported by support. Although a nano wire may contact support in case a nano wire develops by electron beam irradiation, it does not correspond [that this contact was described above " supported" and].

[0009] The metal nano wire of this invention may be divided into a wire part and a support part by the suitable separation approach. The physical separation approaches, such as giving the approaches (centrifugal separation etc.) and vibration using specific gravity as the separation approach, for example, etc. are mentioned.

[0010] The configuration of a metal nano wire is [the exposure reinforcement of an electron ray, and whenever / illuminating-angle] controllable by combining suitably the configurations (pore structure, crystal structure, etc.) of metal ion support, and a presentation.

[0011] Moreover, metal ion support means the thing which made support support a metal ion.

[0012] The gestalt of support has adsorption and ion-exchange ******, and may make a metal ion support beforehand if needed at the time of support composition.

[0013] Support plays a role of a base material of a wire or particle, in case a metal grows as a wire or particle by the exposure of an electron ray. As support, the compound which has NASICON mold structure is mentioned, for example.

[0014] Desirable metal ion support is complex ion support, palladium ion

support, nickel ion support, golden ion support, etc. Still more desirable one is general formula [1]:AgaBcDeSifPgOh. [1]
[B is at least one sort chosen from alkali metals, an alkaline-earth-metal element, copper, zinc, hydrogen, and ammonium, and D is at least one sort chosen from from among the metallic elements which can become the metal ion of 3 - pentavalence. Moreover, the subscripts in a formula are 0<a, 0<=c, 1<a+c<=4, 1<=e<=2, 0<=f<=3, 0<=g<3, and a number that fills 10<=h<=15.] It is the compound come out of and shown.
[0015] In the above-mentioned general formula [1], it is 0<a. Desirable a is a value from which the content of Ag in the compound shown by the general formula [1] becomes more than 0.36 mol %.
[0016] In the above-mentioned general formula [1], B is at least one sort chosen from alkali metals, an alkaline-earth-metal element, copper, zinc, hydrogen, and ammonium. For example, there are alkaline-earth-metal elements, such as alkali metals, such as a lithium, sodium, and a potassium, magnesium, or calcium, copper, and zinc. In these, the copper from the stability and the point which can come to hand cheaply of a compound, zinc, a lithium, sodium, a potassium, hydrogen, and ammonium are desirable.
[0017] In the above-mentioned general formula [1], although it is 1<a+c<=4, it is 1.5 <=a+c<=4 preferably and is 2 <=a+c<=4 more preferably.
[0018] In the above-mentioned general formula [1], D is at least one sort of metallic elements chosen from the group which consists of a metallic element which can become the metal ion of 3 - pentavalence, and when using two or more sorts of metallic elements, it can be used, combining suitably so that the total quantity of each metallic element may be set to e (1<=e<=2). As a trivalent metal element, titanium, a zirconium, germanium, tin, a hafnium, etc. are mentioned as a quadrivalent metal element, and chromium, aluminum, iron, etc. are mentioned for niobium, a tantalum, etc. as a pentavalent metal element. When aluminum, a zirconium, titanium, tin, niobium, etc. are mentioned as a desirable example and the safety of a compound is taken into consideration, iron, a zirconium, or especially titanium is desirable.
[0019] In the above-mentioned general formula [1], although it is 1<=e<=2, it is e= 2 preferably.
[0020] In the above-mentioned general formula [1], although it is 0<=f<=3, it is 0.5<=f<=3 preferably, and is 1<=f<=2.5 more preferably.
[0021] In the above-mentioned general formula [1], although it is 0<=g<3, it is 0< g<=2.5 preferably, and is 0.5<=g<=2 more preferably.
[0022] In the above-mentioned general formula [1], h is suitably decided

according to other amounts of Ag, B, D, Si, and P. It is 10<=h<=15 preferably, and is 11<=h<=13 more preferably.

[0023] As what supplies an electron ray, especially if an electron can be supplied to metal ion support, it will not be restricted. An electron gun is mentioned as an example. As an electron gun, the electron gun of various molds including a thermoelectron gun and a field emission mold electron gun can be used. A thermoelectron gun and a field emission mold electron gun are desirable.

[0024] After an electron ray passes the velocity selector for arranging an electron lens, a deflecting electrode or a deviation electromagnet, and energy if needed, it is made to collide in label, after emanating from an electron gun. Although acceleration voltage is influenced by the degree of vacuum, it is 1kV or more. It is 5kV or more preferably, and is 30-300kV still more preferably. Moreover, although a degree of vacuum is influenced by acceleration voltage, it is 1x10 - 4 or more Pa. It is 1x10-6 to 5x10 to 5 Pa preferably, and is 1x10-6 to 2x10 to 5 Pa still more preferably.

[0025] As equipment for making an electron ray collide in label, an electron microscope, an X-ray microanalyser (EPMA), photoelectron spectroscopy equipment (ESCA), a cyclotron, etc. can be used. Preferably, it is an electron microscope. Also when using these equipments, it is desirable that above-mentioned acceleration voltage and an above-mentioned degree of vacuum are applied. As an electron microscope, a transmission electron microscope (TEM), a scanning electron microscope (SEM), a scanning transmission electron microscope (STEM), etc. can be used. A transmission electron microscope is desirable.

[0026] The metal ion support which has irradiated the electron ray produces a crack on a front face, and a metal nano wire and/or metal nano particle elongate it from the crack. By adjusting the presentation of the exposure condition metallurgy group ion support of an electron ray etc., both metal nano wire and metal nano particle can also be manufactured to coincidence, and it can also manufacture separately. For example, when an electron ray is irradiated at complex ion support, if it is advantageous to manufacture of a silver nano wire if the complex ion content contained in complex ion support is more than 0.36 mol %, and it is less than [0.36 mol %], it will become advantageous to manufacture of silver nano particle.

[0027] The aspect ratio of the metal nano wire of this invention is ten or more, and are 100-100000 preferably.

[0028] 2-500nm of diameters of the metal nano wire of this invention is 5-50nm preferably. Moreover, the conditions (irradiation time,

acceleration voltage, degree of vacuum, etc.) which irradiate the content and electron ray of a metal ion which are contained in metal ion support can adjust the die length of a metal nano wire. Preferably, it is 50nm - 0.5mm still more preferably 20nm - 1mm.

[0029] 2-100nm of particle size of the metal nano particle of this invention is 5-80nm preferably.

[0030] The metal nano wire and metal nano particle of this invention can be used in various fields by using the big surface area, conductivity, and thermal conductivity. For example, it can be used for an electron device ingredient, a catalyst, the template of a carbon nanotube, an alloy ingredient, etc. Preferably, it can be used for a catalyst, an electron device ingredient, etc.

[0031] Although there are a solid phase technique, a wet method, a hydrothermal method, etc. in the approach of compounding the compound shown by the above-mentioned general formula [1] and it is not especially limited to it, as it is the following, for example, it can obtain easily.

[0032] The compound shown by the following general formula [2] is manufactured by mixing the compound containing the compound containing alkali metals or an alkaline-earth-metal element, the compound containing silicon, the compound containing the metallic element which can become the metal ion of 3 - pentavalence, and a phosphoric acid with a suitable mixing ratio, and calcinating this at 1000-1300 degrees C, when compounding by the solid phase technique.

[0033]

B'a+cDeSifPgOh [2]

[B' is at least one sort chosen from the group which consists of alkali metals and an alkaline-earth-metal element, and D, a, c, e, f, g, and h are as above-mentioned.]

In manufacture of the compound of the above-mentioned general formula [2] by the solid phase technique, alkali metal or an alkaline-earth-metal carbonate, a hydrogencarbonate, a hydroxide, a nitrate, a nitride, etc. are illustrated as a compound containing alkali metals or an alkaline-earth-metal element. It is a carbonate, a hydrogencarbonate, and a nitrate preferably, and carbonates, such as a sodium carbonate, potassium carbonate, a calcium carbonate, and a magnesium carbonate, and a sodium nitrate are more desirable.

[0034] In manufacture of the compound of the above-mentioned general formula [2] by the solid phase technique, a silicon dioxide, a silicate, etc. are illustrated as a compound containing silicon. It is a silicon dioxide, a sodium silicate, and colloidal silica preferably, and is a

silicon dioxide more preferably.
[0035] In manufacture of the compound of the above-mentioned general formula [2] by the solid phase technique, the metallic oxide of 3 - pentavalence, a metal hydroxide, a carbonate, etc. are illustrated as a compound containing the metallic element which can become the metal ion of 3 - pentavalence. It is a zirconium dioxide, titanium oxide, tin oxide, a water zirconium dioxide, water titanium oxide, niobium oxide, chromic oxide, a chromium nitrate, an aluminum oxide, etc. preferably, and they are a zirconium dioxide and titanium oxide more preferably.
[0036] In manufacture of the compound of the above-mentioned general formula [2] by the solid phase technique, phosphate, phosphoric-acid hydrogen salt, etc. are illustrated as a compound containing a phosphoric acid. It is sodium phosphate, a phosphoric-acid zirconium, phosphoric-acid titanium, potassium phosphate, dibasic sodium phosphate, a phosphate water ** potassium, phosphate water ** ammonium, etc. preferably, and they are sodium phosphate, a phosphoric-acid zirconium, phosphoric-acid titanium, and phosphate water ** ammonium more preferably.
[0037] The compound which contains alkali metals or an alkaline-earth-metal element when compounding with a wet method, The compound containing the compound containing silicon, the compound containing the metallic element which can become the metal ion of 3 - pentavalence, and a phosphoric acid is mixed with a suitable mixing ratio. Mixture and water can be enclosed with a proof-pressure container, and the compound shown by the above-mentioned general formula [2] can be obtained by making it react under 20-hour hydrothermal conditions preferably at 300 degrees C for 10 to 30 hours.
[0038] In manufacture of the compound of the above-mentioned general formula [2] by the wet method, alkali metal or an alkaline-earth-metal hydroxide, a carbonate, a hydrogencarbonate, a nitrate, etc. are illustrated as a compound containing alkali metals or an alkaline-earth-metal element. It is a carbonate and a nitrate preferably and a sodium silicate, a sodium carbonate, a sodium nitrate, a magnesium nitrate, a calcium nitrate, etc. are more desirable.
[0039] In manufacture of the compound of the above-mentioned general formula [2] by the wet method, silicates, a silicon dioxide, etc. are illustrated as a compound containing silicon. It is a sodium silicate and colloidal silica preferably, and is a sodium silicate more preferably.
[0040] In manufacture of the compound of the above-mentioned general formula [2] by the wet method, the metal salts of 3 - pentavalence,

phosphate, a chloride, a nitrate, etc. are illustrated as a compound containing the metallic element which can become the metal ion of 3 - pentavalence. It is a phosphoric-acid zirconium, zirconium oxychloride, a titanium chloride, an aluminum chloride, an aluminium nitrate, chlorination tin, a tantalum chloride, etc. preferably, and they are an alpha mold-phosphoric-acid zirconium, zirconium oxychloride, and a titanium chloride more preferably.

[0041] In manufacture of the compound of the above-mentioned general formula [2] by the wet method, a phosphoric acid, phosphate, phosphoric-acid hydrogen salt, etc. are illustrated as a compound containing a phosphoric acid. It is a phosphoric-acid zirconium, phosphoric-acid titanium, and sodium phosphate preferably, and they are a phosphoric-acid zirconium and sodium phosphate more preferably.

[0042] In manufacture of the compound of the above-mentioned general formula [2] by the solid phase technique, a wet method, etc., the mixing ratio of these compounds is suitably chosen according to the compound of the general formula [2] made into the purpose. In a solid phase technique For example, a sodium carbonate (Na2CO3), a silicon dioxide (SiO2), By mixing a zirconium dioxide (ZrO2) and an alpha mold-phosphoric-acid zirconium (Zr(HPO4) 2andH2O) so that it may become the mole ratio of 1.25:1.5:1.25:0.75, and calcinating this at 1000-1300 degrees C The compound of the following general formula [3] can be obtained by warming gradually from a room temperature preferably and calcinating at 1000-1300 degrees C.

[0043]

Na2.5Zr2Si1.5P1.5O12 [3]

The compound shown by the general formula [2] obtained by the solid phase technique, the wet method, etc. under a room temperature -100 degree C temperature condition with predetermined acid concentration, for example, the acidic solution which adjusted to 0.1-3N For example, after processing for two - seven days and considering as a proton mold compound, the compound shown by the general formula [1] can be obtained by being immersed in the complex ion content water solution continuously adjusted to predetermined complex ion concentration, for example, 0.1-3N, for example, for two - seven days, and carrying out the ion exchange to it. Under the present circumstances, as an acidic solution to be used, a hydrochloric acid, a nitric acid, etc. are mentioned and a hydrochloric acid is mentioned more preferably. Moreover, as a complex ion content water solution, a silver-nitrate water solution is suitable.

[0044] Moreover, acidic solution processing of the compound shown by the general formula [2] obtained by the solid phase technique, the wet

method, the hydrothermal method, etc. can be omitted, and the compound shown by the general formula [1] can be obtained also by immersing the compound concerned in a complex ion content water solution.
[0045] Furthermore, it adds in the copper ion content water solution which adjusted the above-mentioned proton mold compound to predetermined copper ion concentration, for example, about 0.1-3N, and after supporting a copper ion with agitating for about 1 to 10 hours, the compound shown by the general formula [1] of silver and a copper type can be obtained by carrying out churning processing for about 1 to 10 hours in the complex ion content water solution succeedingly adjusted to about 0.01-3N. Under the present circumstances, as a copper ion content water solution to be used, a copper nitrate, a copper chloride, etc. are raised and a silver-nitrate water solution is suitable as a complex ion content water solution.
[0046] This technique by using suitably a complex ion content water solution, a zinc ion content water solution, an iron ion content water solution, etc. As a zinc ion content water solution which can apply also in case the compound shown by the general formula [1] of a zinc mold, silver and a zinc mold, an iron type or silver, and an iron type is adjusted, and is used in this case A zinc chloride, zinc nitrate, a zinc sulfate, etc. are mentioned, and iron nitrate, a ferric chloride, etc. are mentioned as an iron ion content water solution.
[0047]
[Effect of the Invention] By irradiating an electron ray at metal ion support, it becomes possible to manufacture a metal nano wire and/or metal nano particle, without using mold or ultra-fine processing technology.
[0048]
[Example] Example of manufacture 1Ag2.3 Na0.2 Zr2 Si 1.5P1.5O12 In the disodium hydrogenphosphate (Na2HPO4) water solution of 0.288 mols/l. of manufactures, zirconium oxychloride (ZrOCl2.8H2O), A sodium silicate (Na2O and 3SiO2) and sodium-hydroxide (NaOH) mixed liquor Zr:Si :P = after performing coincidence dropping and rinsing and drying the produced reactant by the mole ratio used as 2:1.5:1.5, by calcinating at 1200 degrees C The sample (NCC-Na is called hereafter) of the sodium mold expressed with Na2.5 Zr2 Si 1.5P1.5O12 was obtained.
[0049] It protonated by processing obtained NCC-Na with a hydrochloric acid. Namely, 3g NCC-Na and 1000ml 1 N-HCl were mixed, and it agitated at the room temperature for 3 hours. The sample (NCC-H is called hereafter) of the proton mold expressed with H2.5 Zr2 Si 1.5P1.5O12 was obtained by filtration, washing, and desiccation after churning.

[0050] It added to 300ml of 0.1-N silver nitrate solutions, and 3.0g of obtained NCC-H was agitated at the room temperature for 3 hours. The silver type sample expressed with Ag2.3 Na0.2 Zr2 Si1.5P1.5 O12 was obtained by filtration, washing, and desiccation after churning. The quantum of the complex ion was carried out by atomic absorption spectrophotometry, and it was computed as an amount of complex ion exchange per 1g of support from the difference of the initial concentration of complex ion, and the equilibrium concentration after the ion exchange.
[0051] NCC-H (sample of the proton mold expressed with H2.5 Zr2 Si 1.5P1.5O12) was obtained like example of manufacture 2 example 1.
[0052] After adding 2g NCC-H in 200ml of 0.2 copper-nitrate water solutions of M and agitating at a room temperature for 3 hours, the copper support sample was prepared through filtration, rinsing, and desiccation using 1.0-micrometer membrane filter.
[0053] Then, after adding 1.9g of copper support samples in 200ml of 0.01-N silver-nitrate water solutions and agitating for 30 minutes at a room temperature, the sample of silver and a copper type expressed with Ag0.587 Cu0.141H1.772 Zr2 Si 1.5P1.5O12 was obtained through filtration, rinsing, and desiccation using 1.0-micrometer membrane filter.
[0054] NCC-H (sample of the proton mold expressed with H2.5 Zr2 Si 1.5P1.5O12) was obtained like example of manufacture 3 example 1.
[0055] After adding 2g NCC-H in 200ml of 0.2 ferric-chloride water solutions of M and agitating at a room temperature for 3 hours, the iron support sample was prepared through filtration, rinsing, and desiccation using 1.0-micrometer membrane filter.
[0056] Then, after adding 1.9g of iron support samples in 200ml of 0.01-N silver-nitrate water solutions and agitating for 30 minutes at a room temperature, the sample of silver and an iron type expressed with Ag0.688 Fe1.276H0.536 Zr2 Si 1.5P1.5O12 was obtained through filtration, rinsing, and desiccation using 1.0-micrometer membrane filter.
[0057] Using example 1 transmission electron microscope, in the silver type sample (Ag content: 3.20 mmol/g) obtained in the example 1 of manufacture, the electron ray was irradiated on condition that the following, and the silver nano wire was obtained (drawing 1). The diameter of the obtained silver nano wire was about 50nm, and die length was about 10 micrometers.
acceleration voltage: -- 300kV degree of vacuum: -- 1 - 3x10-5Pa irradiation time: -- quantitative analysis of the silver nano wire part obtained in the example 2 example 1 for about 10 seconds and a support part was carried out. The energy-dispersive-X-ray-spectroscopy machine

attached in the transmission electron microscope was used for quantitative analysis. As a result of quantitative analysis, Ag content in a silver nano wire was 99.35-mol %, and Ag content in support was 6.69-mol %.

[0058] Using example 3 scanning electron microscope, in the silver type sample (Ag content: 3.20 mmol/g) obtained in the example 1 of manufacture, the electron ray was irradiated on condition that the following, and the silver nano wire was obtained (drawing 2). The diameter of the obtained silver nano wire was about 10nm, and die length was about 1 micrometer.

acceleration voltage: -- 5kV degree of vacuum: -- 1x10-5Pa irradiation time: -- to the silver type compound (Ag content: 3.20 mmol/g) obtained in the example of manufacture using example 4 scanning electron microscope for about 30 seconds, the electron ray was irradiated on condition that the following, and a silver nano wire and silver nano particle were obtained (drawing 3 and drawing 4). The diameter of the obtained silver nano wire was about 40nm, and die length was about 50 micrometers. Moreover, the particle size of the obtained silver nano particle was 5-80nm.

acceleration voltage: -- 30kV degree of vacuum: -- 1x10-5Pa irradiation time: -- about 30 seconds

---

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the electron microscope photograph in which the silver nano wire and support which were obtained in the example 1 are shown.

[Drawing 2] It is the electron microscope photograph in which the silver nano wire and support which were obtained in the example 3 are shown.

[Drawing 3] It is the electron microscope photograph in which the silver nano wire and support which were obtained in the example 4 are shown.

[Drawing 4] It is the electron microscope photograph in which the silver nano particle and support which were obtained in the example 4 are shown.
